FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Self-Interaction Correction Constraint and Rotation Symmetry for Molecules and Solids

Sheng Bi

Supervised by
Igor Ying Zhang, Christian Carbogno, and Matthias Scheffler

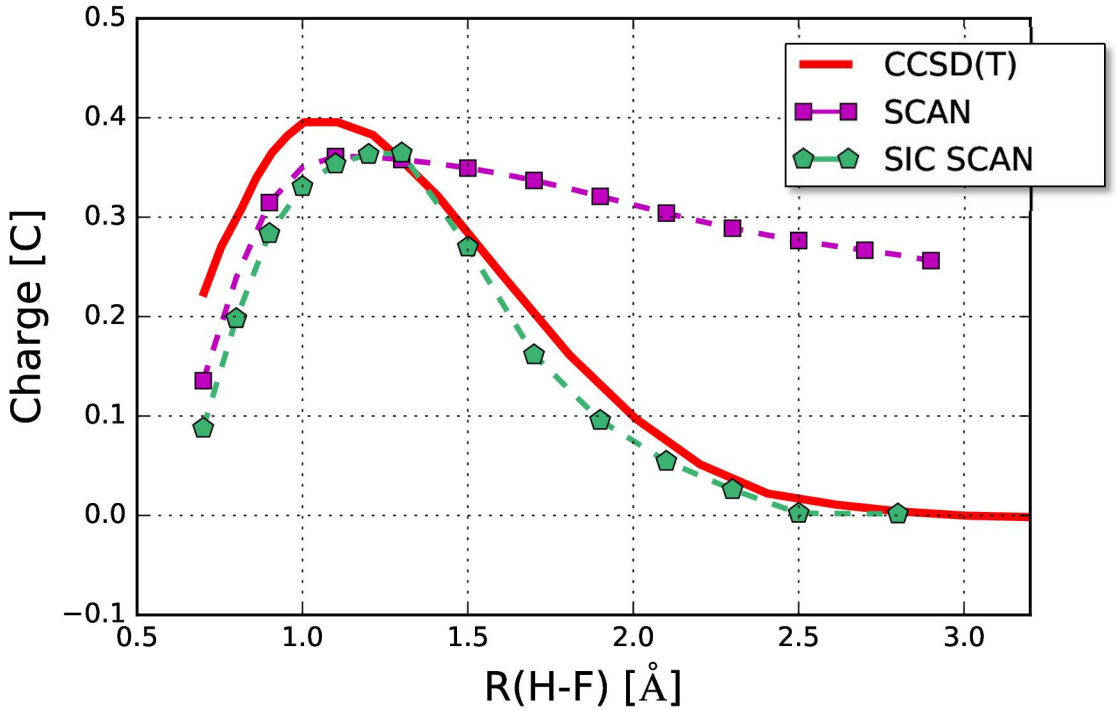
Previous Results

$-\epsilon^{\mathrm{HOMO}}$ = first ionization potential

	HOMO Energy $-\epsilon^{\mathrm{HOMO}}$ [eV]		Ionization Potential [eV]
	SCAN	SIC SCAN	Expt.[1]
N2	10.75	17.37	15.56
O2	7.55	15.47	12.07
H2O	7.61	14.40	12.62
CO	9.56	15.37	14.10
C2H2	7.40	12.25	10.51
MAE	4.40	2.00	

MAE : mean absolute error

H^{+q}-F^{-q}



1. K. Watanabe, T. Nakayama, and J. Mottl, J. Quant. Spectrosc. Radiat. Transfer **2**, 369 (1962).

Perdew and Zunger SIC (PZ-SIC)

Perdew and Zunger SIC (PZ-SIC)

- SIC One-Electron Hamiltonian

$$E_{SIC} = E_{KS} - \sum_i E_{es}[n_i^{LO}] + E_{xc}[n_i^{LO}]$$

$$\delta E_{SIC} = 0 \longrightarrow \hat{h}^{SIC} = \underbrace{h^{KS}[n]}_{\text{total density dependent}} - \sum_i v^{SIC}[n_i^{LO}]|\phi_i^{LO}\rangle\langle\phi_i^{LO}|$$

1. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

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- SIC One-Electron Hamiltonian

$$\hat{h}^{SIC} = h^{KS}[n] - \sum_i \underline{v^{SIC}[n_i^{LO}]}|\phi_i^{LO}\rangle\langle\phi_i^{LO}|$$

SIC potential $v^{SIC}[n_i^{LO}] = \dfrac{\delta E_{es}[n_i^{LO}] + E_{xc}[n_i^{LO}]}{\delta n_i^{LO}}$

Localized Orbitals(LOs) dependent $n_i^{\mathrm{LO}} = |\phi_i^{\mathrm{LO}}|^2$

1. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

Perdew and Zunger SIC (PZ-SIC)

Perdew and Zunger SIC (PZ-SIC)

$$\hat{h}^{SIC} = h^{KS}[n] - \sum_i v^{SIC}[n_i^{LO}]|\phi_i^{LO}\rangle\langle\phi_i^{LO}|$$

diagonalization

$$\hat{h}^{SIC}|\psi_m\rangle = \epsilon_m|\psi_m\rangle$$

quasi-particle orbitals (named KS orbitals)

energy levels

1. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

SIC Constraint

FHI-aims

the numeric atom-centered orbital (NAO) $\varphi_l(r)(l = 1, \cdots, N_b)$

$$\psi_m = \sum_{l=1}^{N_b} c_{ml}\varphi_l$$

$$\hat{h}^{SIC}|\psi_m\rangle = \epsilon_m|\psi_m\rangle$$

matrix form $\downarrow$

$$\sum_l \langle\varphi_t|\hat{h}^{SIC}|\varphi_l\rangle c_{lm} = \epsilon_l \sum_t s_{tl}c_{lm}$$

1. V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comput. Phys. Commun. 180, 2175 (2009).

Perdew and Zunger SIC (PZ-SIC)

Why LOs are introduced? **PZ-SIC : remove all single-electron self-interaction errors**

1. the SIC total energy is global minimum.

Carbon as example :

$$E_{SIC}[|\psi_m|^2] = -1027.92eV$$
$$E_{SIC}[n_i^{LO}] = -1028.85eV$$

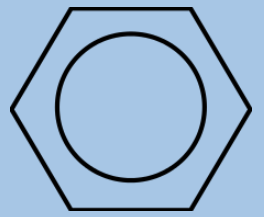
$$E_{SIC}[n_i^{LO}] = E_{KS} - \sum_i E_{es}[n_i^{LO}] + E_{xc}[n_i^{LO}]$$

Perdew and Zunger SIC (PZ-SIC)

1. global minimum

2. Hamiltonion is Hermitian

$$\hat{h}'^{SIC} = \sum_i (h^{KS}[n] - v^{SIC}[n_i])|\psi_i\rangle\langle\psi_i|$$

Benzene 

$$\left(\hat{h}'^{SIC}\right)^{\dagger} \neq \hat{h}'^{SIC}$$

$$\downarrow$$

eigenvalues are not real ✗

SIC constraint : Hermitian Operator

$$\hat{h}^{SIC} = \sum_i \left(h^{\mathrm{DFT}}[n] + v^{\mathrm{SIC}}[n_i^{LO}]\right) |\phi_i^{LO}\rangle\langle\phi_i^{LO}|$$

SIC constraint : $\left(\hat{h}^{SIC}\right)^\dagger = \hat{h}^{SIC}$

$$\Downarrow$$

$$\langle\phi_i^{LO}|v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}]|\phi_j^{LO}\rangle = 0$$

SIC constraint : Hermitian Operator

$$\hat{h}^{SIC} = \sum_i \left(h^{\mathrm{DFT}}[n] + v^{\mathrm{SIC}}[n_i^{LO}]\right) |\phi_i^{LO}\rangle\langle\phi_i^{LO}|$$

SIC constraint : $\left(\hat{h}^{SIC}\right)^\dagger = \hat{h}^{SIC}$

$$\langle\phi_i^{LO}|v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}]|\phi_j^{LO}\rangle = 0$$

Newton method requires $\dfrac{d\left(v^{SIC}[n_j^{LO}]\right)}{d\phi_j^{LO}}$ lots of work

SIC constraint : Hermitian Operator

artificial weights $w_{j+1} \gg w_j \gg |\langle \phi_j^{LO} | v^{SIC}[n_j^{LO}] | \phi_j^{LO} \rangle|$

$$\langle \phi_i^{LO} | v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}] + w_j \delta_{ij} | \phi_j^{LO} \rangle = \langle \phi_i^{LO} | w_j \delta_{ij} | \phi_j^{LO} \rangle$$

Eigen Problem $\sum_i \left(v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}] + w_j \delta_{ij} \right) |\phi_j^{LO}\rangle = w_j |\phi_j^{LO}\rangle$

SIC constraint : Hermitian Operator

Eigen Problem

$$n_i^{LO}$$

$$\downarrow$$

$$v^{SIC}[n_i^{LO}]$$

$$\downarrow$$

$$\sum_i \left(v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}] + w_j \delta_{ij}\right) |\phi_j^{LO}\rangle = w_j |\phi_j^{LO}\rangle$$

$$\downarrow$$

$$\phi_j^{LO}$$

SIC constraint : initial Guess

1. gloable minimum

2. Hamiltonion Hermitian Operator

$$n_i^{LO}$$

$$\downarrow$$

$$v^{SIC}[n_i^{LO}]$$

$$\downarrow$$

Eigen Problem $$\sum_i \left(v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}] + w_j\delta_{ij}\right)|\phi_j^{LO}\rangle = w_j|\phi_j^{LO}\rangle$$

$$\downarrow$$

$$\phi_j^{LO}$$

SIC constraint : initial Guess

1. gloable minimum

2. Hamiltonion Hermitian Operator

initial guess of LO :

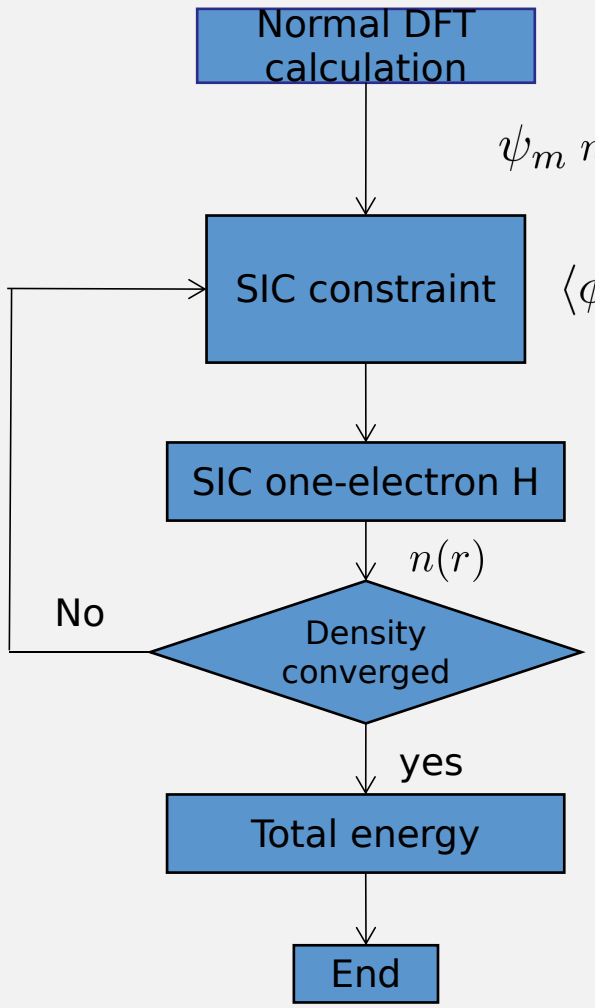
80% atomic orbital + 20% KS orbitals

H_2 : KS orbitals $\sigma_{s\uparrow}, \sigma_{s\downarrow}$

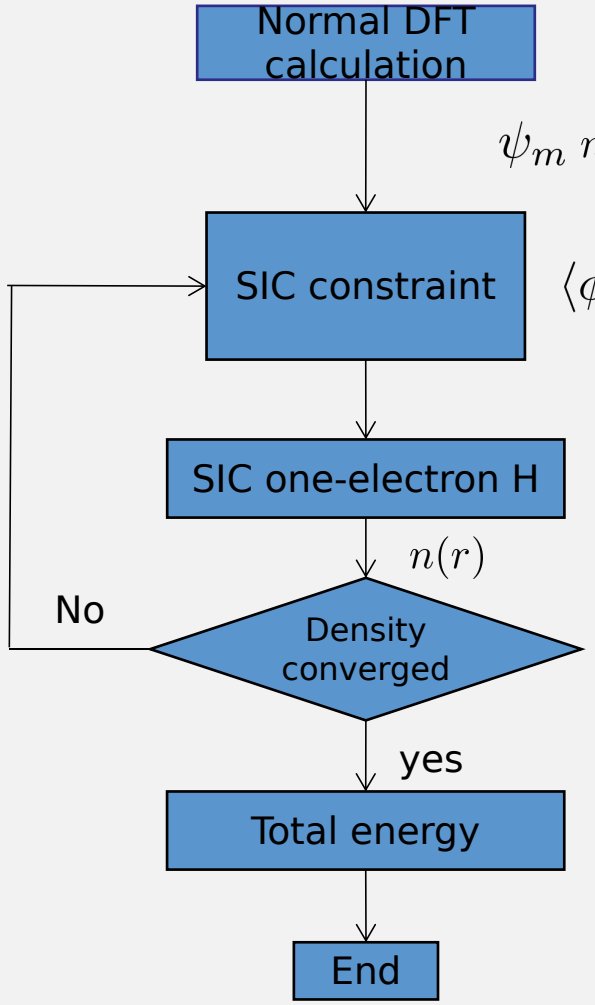
$$\phi_{1\uparrow}^{LO} = 0.8\phi_{1s}^{at}(r - R_1) + 0.2\sigma_{s\uparrow}$$

$$\phi_{1\downarrow}^{LO} = 0.8\phi_{1s}^{at}(r - R_2) + 0.2\sigma_{s\downarrow}$$

Implementation



Implementation



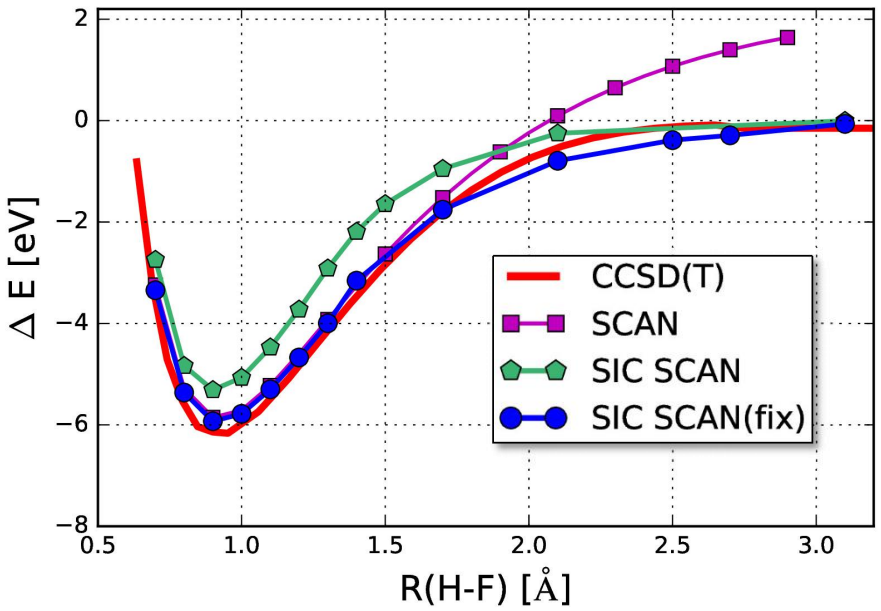
$$\langle \phi_i^{LO} | v^{SIC}[n_i^{LO}] - v^{SIC}[n_j^{LO}] | \phi_j^{LO} \rangle = 0$$

$$\hat{h}^{SIC} | \psi_m \rangle = \epsilon_m | \psi_m \rangle$$

SIC : $E_{SIC} = E_{KS} - \sum_i E_{es}[n_i^{LO}] + E_{xc}[n_i^{LO}]$

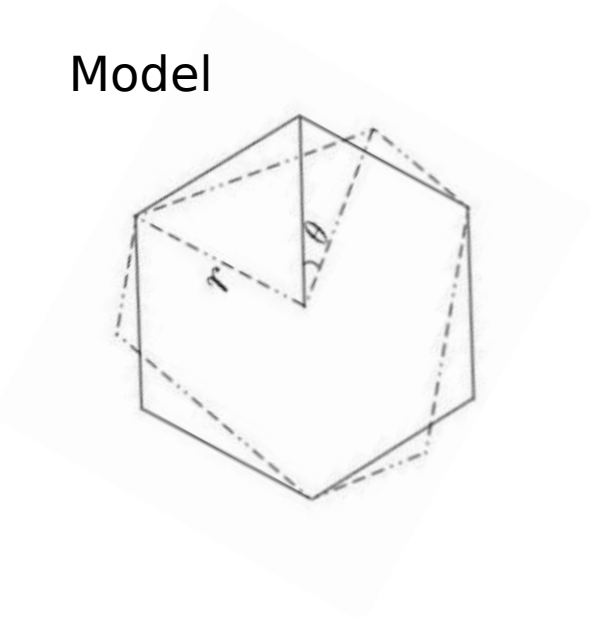
SIC(fix) : $E_{KS}[n]$

H^{+q}-F^{-q}

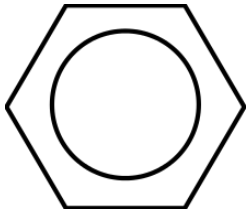


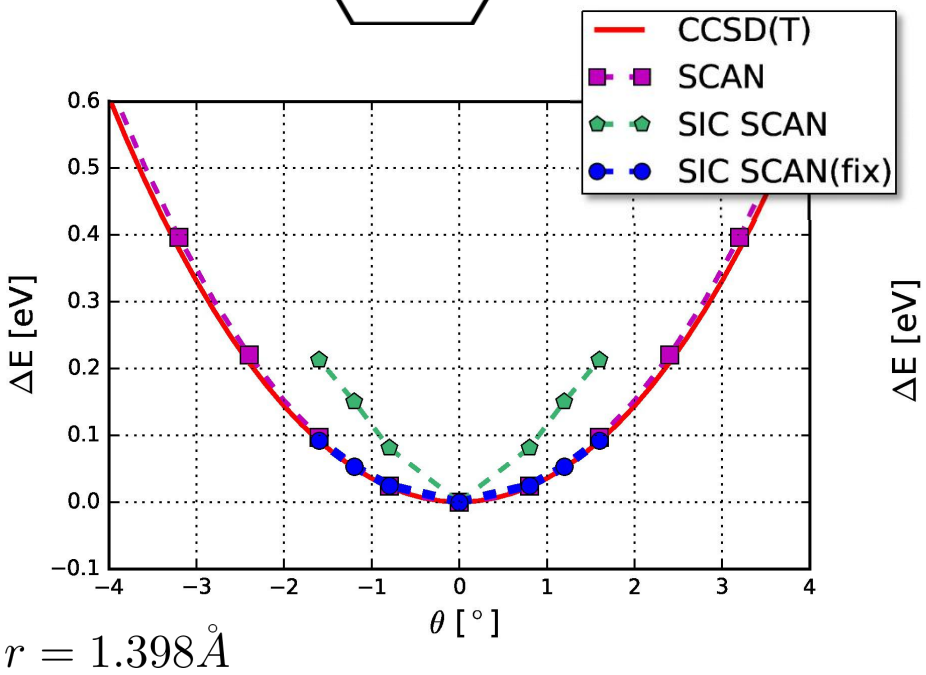
Rotation Symmetry : Benzene and H6

Model



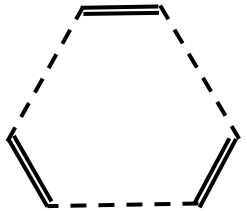
Benzene

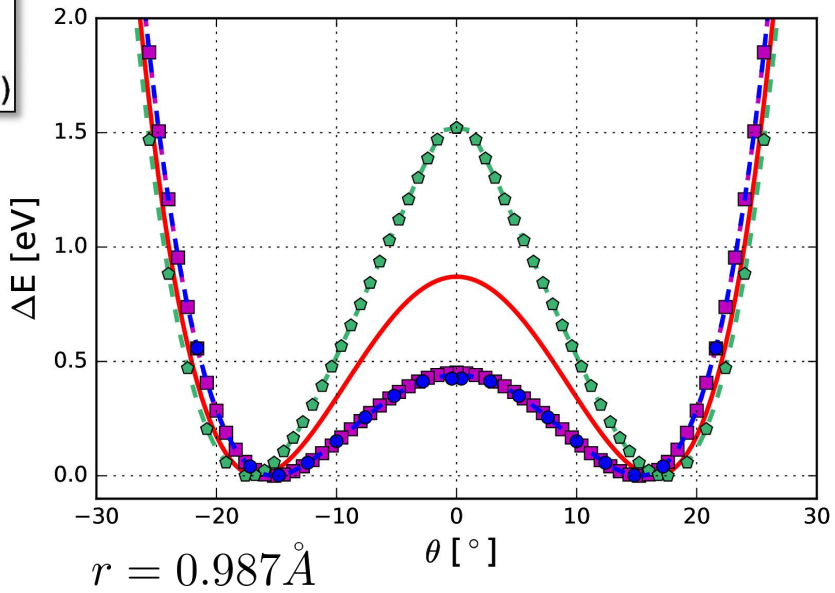




$r = 1.398\mathring{A}$

H6



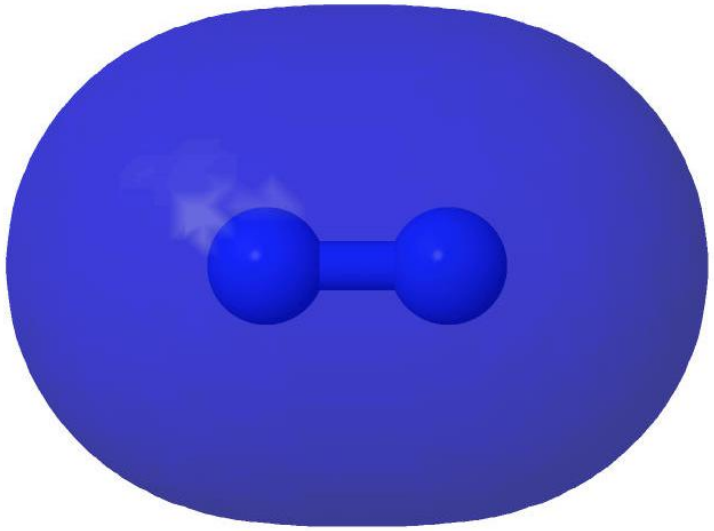


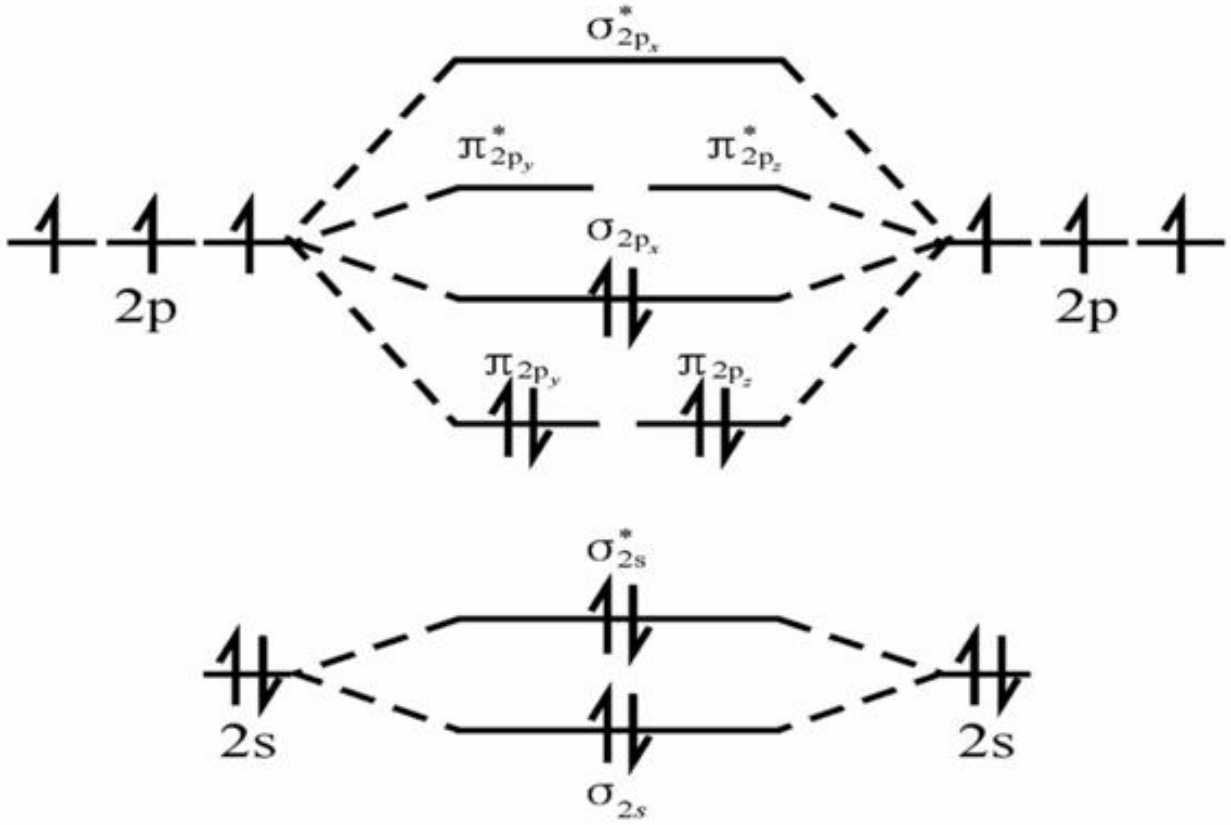
$r = 0.987\mathring{A}$

1. S. Lehtola, M. Head-Gordon, and H. Jónsson, J. Chem. Theory Comput. **12**, 3195 (2016).

Rotation Symmetry : Diatomic Molecule

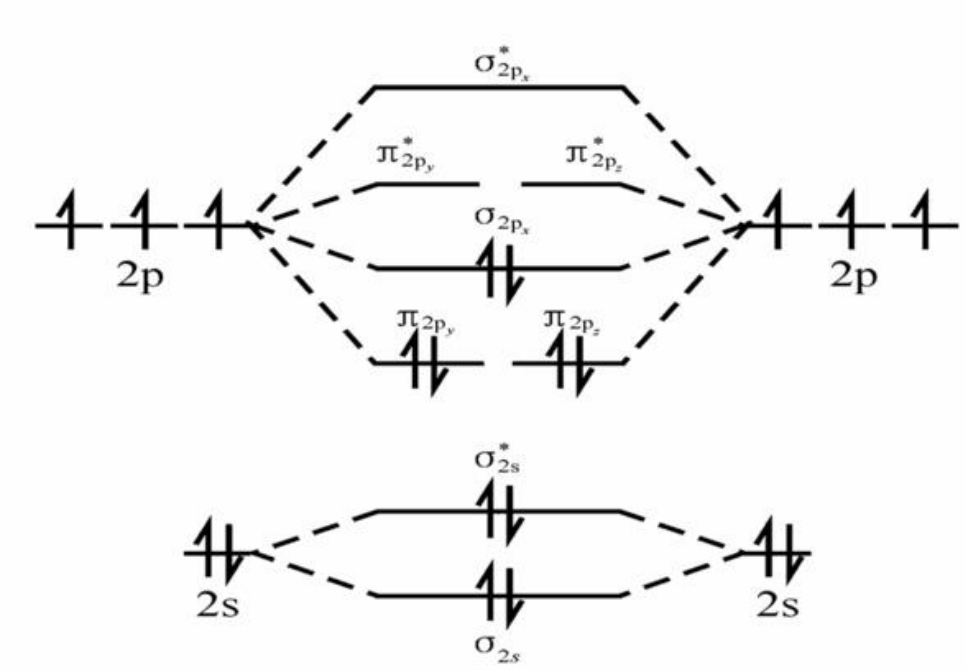
N_2





Rotation Symmetry : Diatomic Molecule

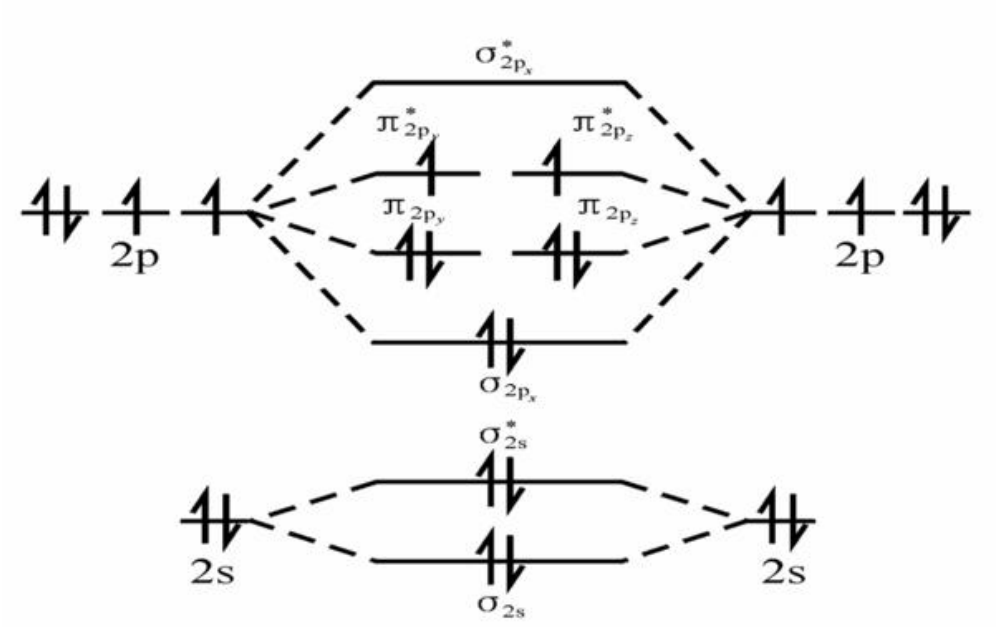
N_2



spin up	SCAN	SIC SCAN
σ_{2p_x}	-10.75	-17.37
$\pi_{2p_y}\pi_{2p_x}$	-11.99	-17.74
σ^*_{2s}	-14.10	-21.24
σ_{2s}	-14.29	-36.89

Rotation Symmetry : Diatomic Molecule

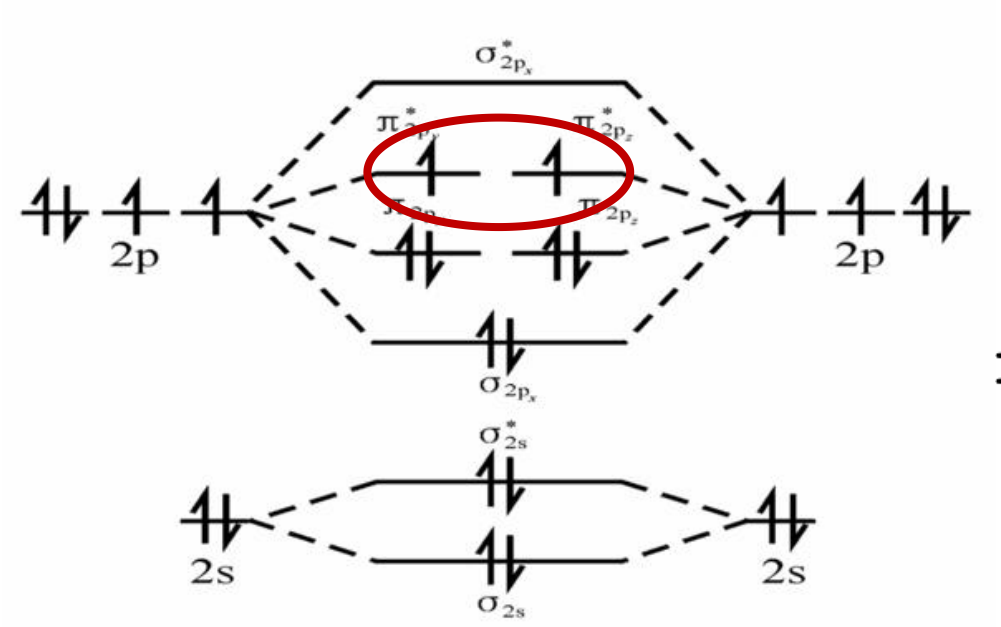
O_2



spin up	SCAN	SIC SCAN
$\pi^*_{2p_y}\pi^*_{2p_x}$	-7.55	-15.48
σ_{2p_x}	-14.10	-21.97
$\pi_{2p_y}\pi_{2p_x}$	-14.36	-22.40
σ^*_{2s}	-22.00	-31.30
σ_{2s}	-34.40	-43.66

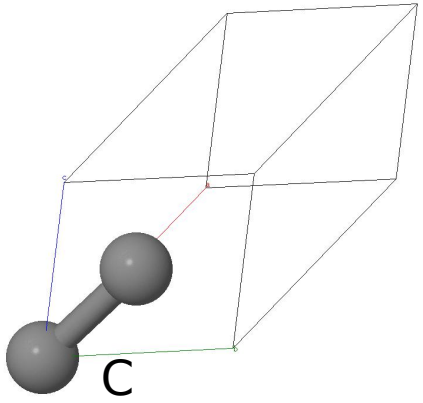
Rotation Symmetry : Diatomic Molecule

$$O_2$$



$$= |\pi_\uparrow\rangle \qquad |g.s.\rangle = \frac{1}{\sqrt{2}}(|\pi_\uparrow\rangle + |\pi_\downarrow\rangle)$$

SIC for Solid : Diamond



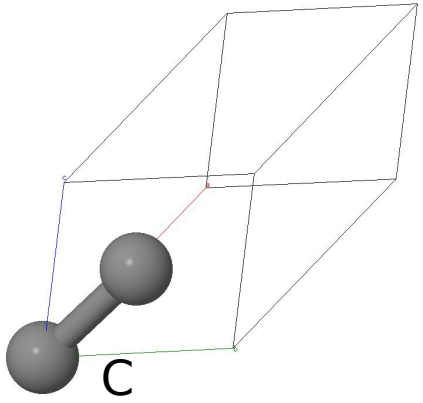
$|a| = |b| = |c| = 2.522\mathring{A}$

K points : $2 \times 2 \times 2$

	expt.	SCAN	SIC SCAN
Indirect Gap (eV)	5.49	4.41	5.04

1. P. Y. Yu and M. Cardona, Fundamentals of Semiconductions (Springer-Verlag, Berlin, 2001)

SIC for Solid : Diamond



$|a| = |b| = |c| = 2.522\mathring{A}$

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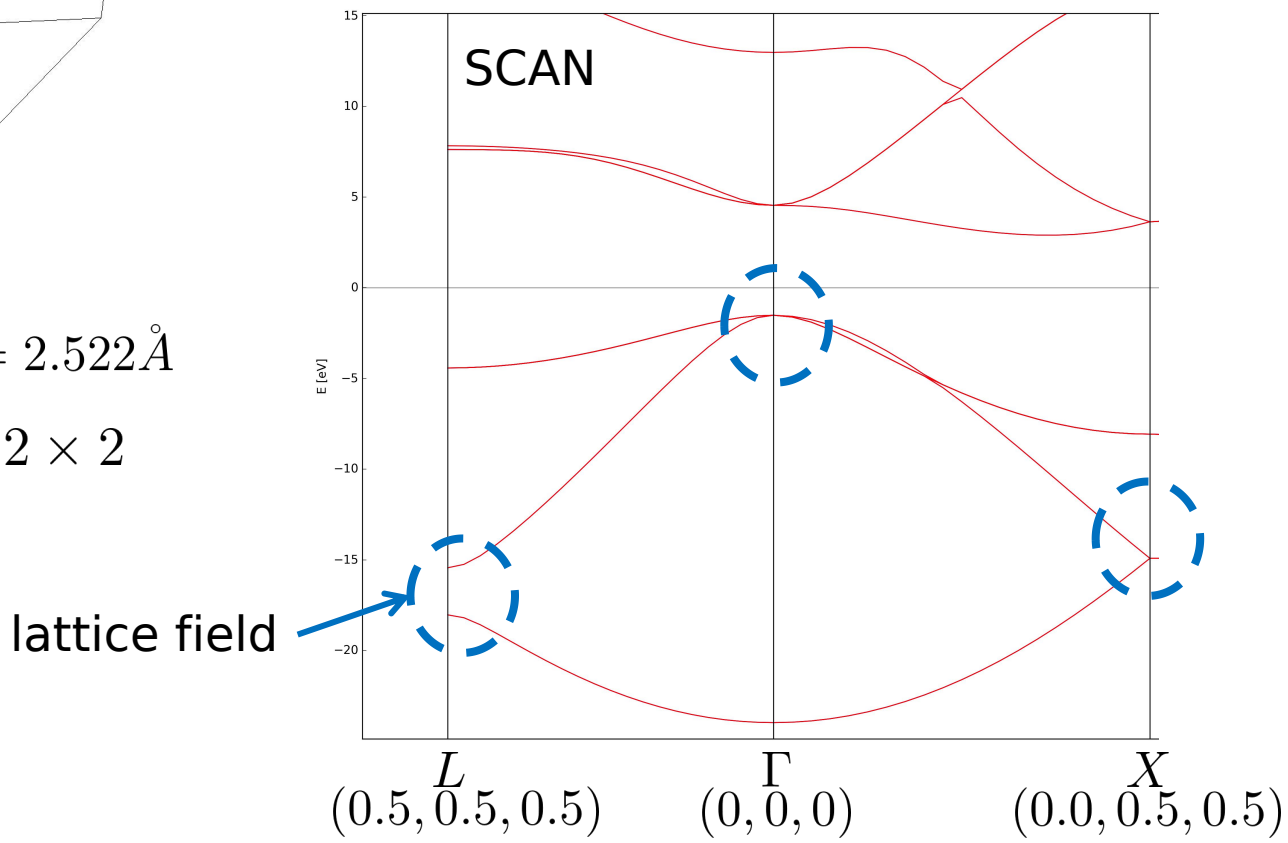
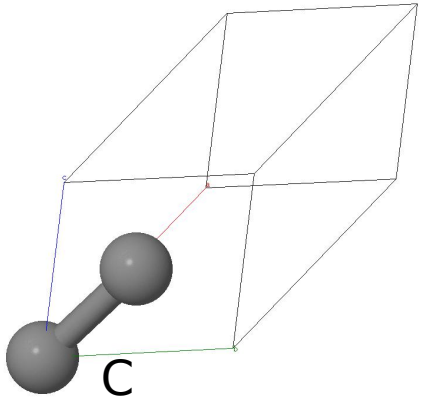


SIC for Solid : Diamond



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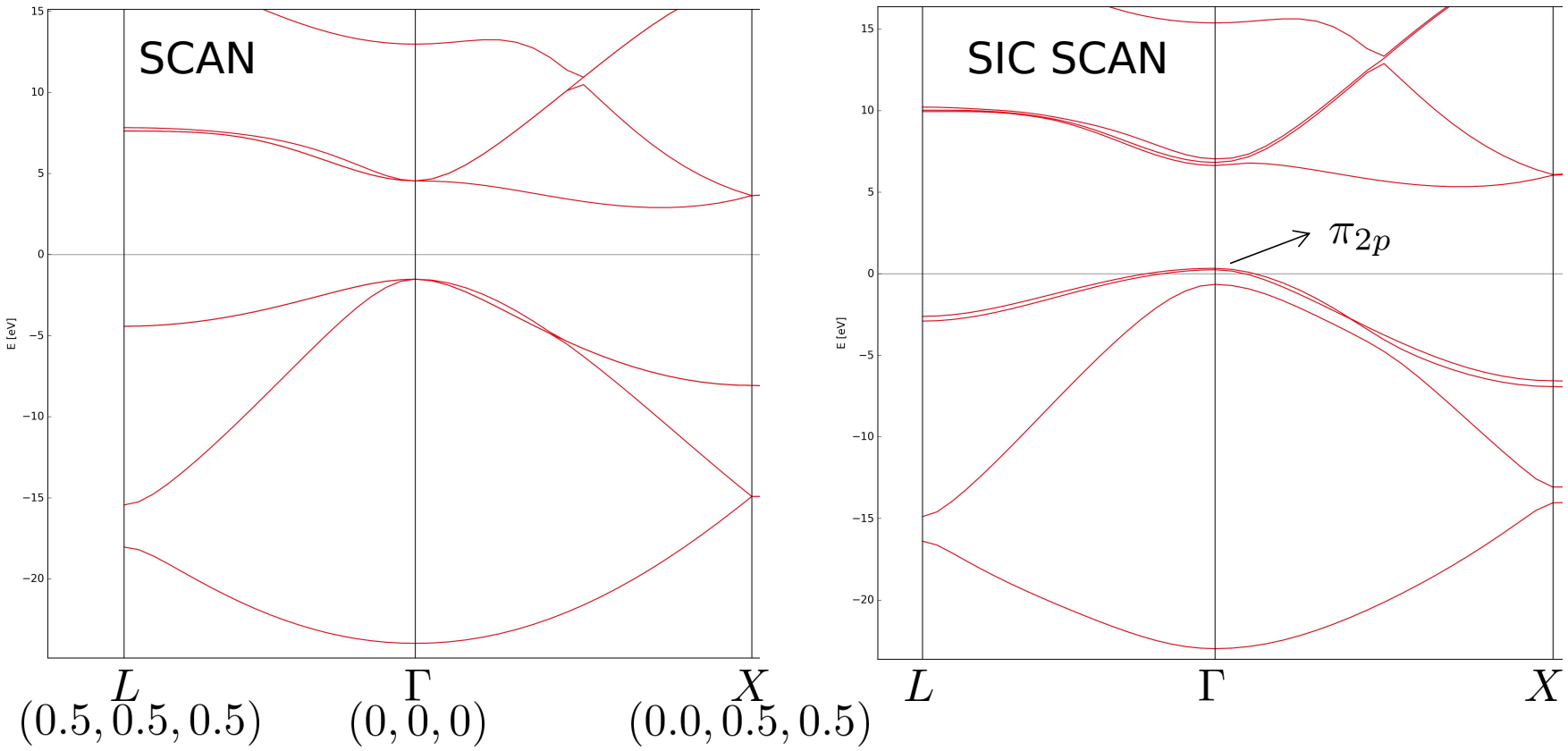

Summary

- PZ-SIC constraint can be transformed to an eigen problem
- ground state symmetry is correct for diatomic molecules
- The band structure of diamond is basically right,
  but still has some problems

Next steps :

- improve the band structure
- try more systems, like Si, c-BN

Thank you